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DISEQUILIBRIUM CONDENSATION ENVIRONMENTS IN SPACE: A FRONTIER IN THERMODYNAMICS*

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Abstract. Quasi-steady states with a disequilibrium between the gas phase kinetic temperature and the condensed phase internal temperature appear to be the norm of condensation environments in space. Such states may constitute Prigogine dissipative structures.

1. Introduction

The processes of formation of dust particles from a gas phase in an open space environment and in an idealized laboratory enclosure may differ significantly in their physical characteristics. The reason for this is that unlike the latter environment, the former is usually characterized by thermal (and hence thermodynamic) disequilibrium. In addition, most condensation environments in space are characterized by appreciable degrees of ionization of the gas phase. These two effects can give rise to interesting modifications of the equilibrium thermodynamics of condensation applicable to the laboratory environment. Any such modifications remain largely unexplored to date, although the literature on the process of condensation in space today is fairly extensive. In this paper we present a brief discussion of the thermal disequilibrium aspect of the problem in an effort to draw attention to the space condensation environment as an interesting arena for application and extension of the ideas and formalisms of nonequilibrium thermodynamics.

An extensive discussion of the physical properties of the condensation environments in space has been presented elsewhere (De and Arrhenius, 1979), wherein pertinent literature has also been cited. Ionization effects (plasma effects) that influence the process of condensation have been discussed in this reference, and also by Mendis (1979).

2. Thermal Disequilibrium: A Norm of Space Condensation Environments

An isolated cloud of gas and dust in the otherwise relatively empty space (the intercloud medium) represents a thermodynamic system in which an equality – or even a near-equality – of the gas phase *kinetic* temperature T_k and the condensed phase

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1979Ap&SS..65..191D

(dust grains) *internal* temperature T_g hardly ever obtains. Instead, thermal quasi-steady states are possible with $T_g \neq T_k$, where the rate of radiative heat loss of a grain is balanced by the rate of heat gain from the impinging gas molecules and the ambient radiation field. The existence of such states is easy to appreciate in the case of a cloud transparent in the wavelengths (predominantly in the infrared) in which the grains emit and absorb most of the energy (Lehnert, 1970; Arrhenius and De, 1973; De, 1977a). In this case the grains radiate essentially directly into the cold intercloud medium, and thus assume a temperature that is cooler than the ambient gas kinetic temperature if this is well above the temperature of the intercloud radiation field. It has been suggested, however, that if the cloud were opaque in the relevant wavelengths, then an equality between T_k and T_g would be ensured – allowing one to apply equilibrium thermodynamics in treating the problem of condensation in such a cloud (Lewis, 1974). Lewis's own argument is, however, based on a simple logical fallacy. He first *assumes* thermal equilibrium, and eventually claims to have *proved* its existence. The logic of this argument, when properly invoked, would be that in the opaque interior of the cloud, the radiation field is enhanced – especially in the infrared wavelengths – by the trapping of radiation from the grains. This would cause the grains in the interior of the cloud to be much hotter than those near the cloud boundary, and conceivably, the grain temperature in the interior could approximate the gas temperature. To examine this proposition, we shall study below the depth-dependent temperature profile of grains in an opaque cloud.

Figure 1 is a sketch showing a dust grain located at a depth h below the freely radiating surface of a cloud which, for the purpose of illustrative calculations to be

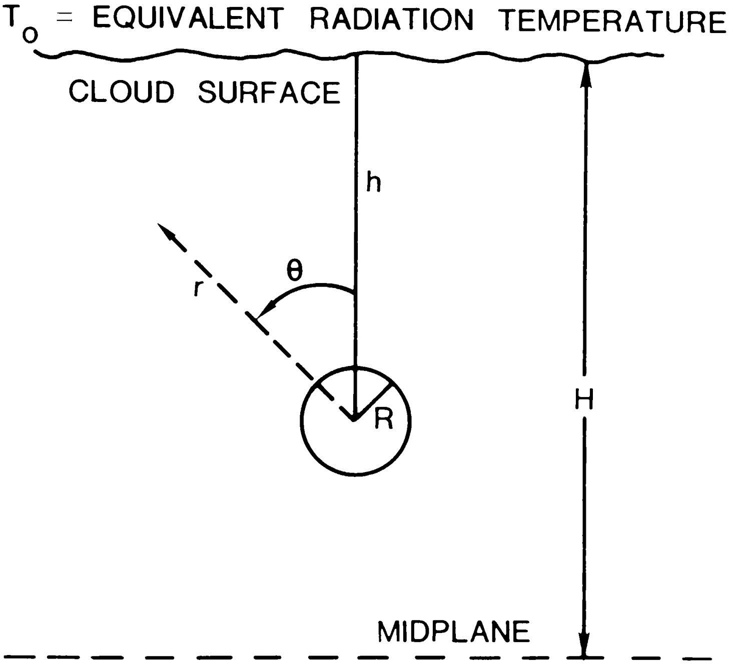

Fig. 1. Sketch of a section of a disk-shaped dust cloud with a mid-plane of symmetry.

1979Ap&SS..65..191D

presented later, is assumed to be roughly disk-shaped with a midplane of symmetry. The definition of a cloud surface is somewhat arbitrary, and we shall later avoid this arbitrariness by assuming that the gas density decreases linearly from a value $N = N_0$ at the midplane to $N = 0$ at the surface. The gas is assumed to be entirely molecular hydrogen. Outside the cloud boundary, the temperature T_0 characterizes the local radiation field – deriving from radiation from neighboring stars (but not the cloud itself). This temperature is defined as that which a blackbody in the region of the grain would attain if it did not receive any heat from the cloud. The grains, with a number density $n(\mathbf{r})$, are all assumed to be spherical black bodies with radius a. Under these conditions, we find that the grain temperature at any point in the cloud is given by the convergent solution of the iteration relation:

$$\begin{aligned}\sigma T^4_{g,(i+1)} &= \sigma T_0^4 + 2CNVk(T_k - T_{g,(i+1)}) + \\ &+ \tfrac{1}{2}\pi\sigma a^2 \int_0^\infty \int_0^\pi n(\mathbf{r})[T_{g,(i)}(\mathbf{r})]^4 \times \\ &\times \exp\left\{-\int_0^r \pi a^2 n(\mathbf{r})\,\mathrm{d}r\right\} \sin\theta\,\mathrm{d}\theta\,\mathrm{d}r, \end{aligned} \tag{1}$$

where σ is the Stefan–Boltzmann constant, k the Boltzmann constant, C the thermal accommodation coefficient, $V\ (= (kT_k/2\pi m)^{1/2})$ the average impingement velocity of the gas molecules (with m the molecular mass), and the subscript i refers to the ith iteration. In the above equation the left-hand side is the heat loss rate of a grain per unit area of grain surface. The first term on the right-hand side is the rate of heat gain from the local radiation field; the second term is the rate of heat gain from the impacting gas molecules; and the last term is the rate of heat gain by the grain in question from all the other grains surrounding it. The exponential term takes care of the fact that the radiation from the grains at location $\mathbf{r}$ becomes attenuated by the intervening grains in reaching the grain in question.

The method of solving Equation (1) is first to neglect the last term and obtain a numerical solution for T_g. Since this solution refers to a case where a given grain does not receive any radiation from the other grains, it gives us the grain temperature in a region that is fully transparent for the escape of infrared radiation. This case has been discussed earlier (Lehnert, 1970; Arrhenius and De, 1973; De, 1977a). This transparent solution constitutes $T_{g,(1)}$ for our iterations. We next enter $T_{g,(1)}$ in the last member of Equation (1), and solve the equation in its entirety to obtain $T_{g,(2)}$. The iterations are then continued until the successive iteration values of $T_{g,(i)}$ do not differ significantly. In this way we obtain a self-consistent solution for the disequilibrium steady state.

As a numerical illustration of the above discussion, we have chosen the much discussed primitive solar nebula where traditionally a complete thermal equilibrium has been assumed – especially in the context of the study of formation of meteorites (see, e.g., review by Barshay and Lewis, 1976). The nebula is visualized as a disk-

1979Ap&SS..65..191D

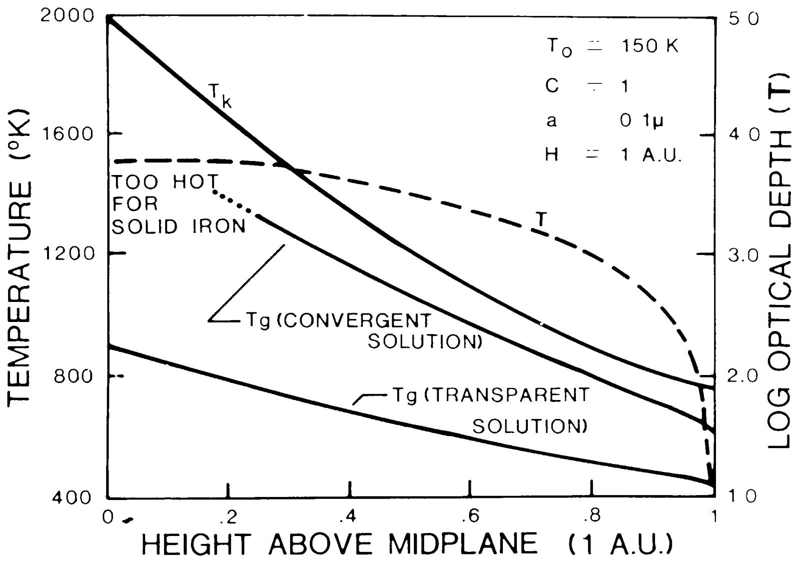

Fig. 2. Gas and grain temperatures as a function of depth in the cloud of Figure 1. Also shown is the optical depth T in the cloud due to dust.

shaped cloud around the Sun (or protosun), and we consider roughly the present asteroidal region (which is also often suggested to be the meteorite formation region). The grains are assumed to be metallic iron (with $a = 0.1$ μ) which, with a relative abundance of 10^{-5} in the nebula, is assumed to be fully condensed wherever the grain temperature is below the condensation temperature of iron. We have assumed, somewhat arbitrarily but roughly in keeping with popular nebular models invoked in meteoritic studies (*op. cit.*), that the temperature T_k decreases from 2000 K at the midplane to 1/e times this value at the surface, while the density N decreases linearly from 10^{15} cm^{-3} at the midplane to 0 at the surface. Other parameters are indicated in Figure 2. Also presented in this figure are the infrared optical depths in the nebula. Note that the condensation temperature of iron under the given conditions is around 1400 K (De, 1977b), so that solid grains cannot exist near the midplane.

While the above calculations are of a preliminary nature and several next-order refinements are required (some of which we have discussed elsewhere; see, e.g., De, 1977a; De and Arrhenius, 1979), the general conclusion appears to be valid that even at large infrared optical depths ($\sim 10^3$–10^4), thermal equilibrium is not attained.

For the sake of completeness we should also discuss the dependence of the T_k–T_g relationship on the gas density. This dependence is shown in Figure 3 (calculated from Equation (1) without the opacity term). The densities at which a near-equality of T_k and T_g obtains are rather high for known or physically realistic cosmic gas-dust environments – certainly for the peripheral regions of the nebula. The other situations in which equilibration may be approached are: (i) larger cloud dimension H (see Figure 1); and (ii) large gaseous infrared opacity. In the former case equilibration will be achieved near the midplane, but disequilibrium will prevail elsewhere. In the second case – in the present example, for instance – the gaseous opacity would

1979Ap&SS..65..191D

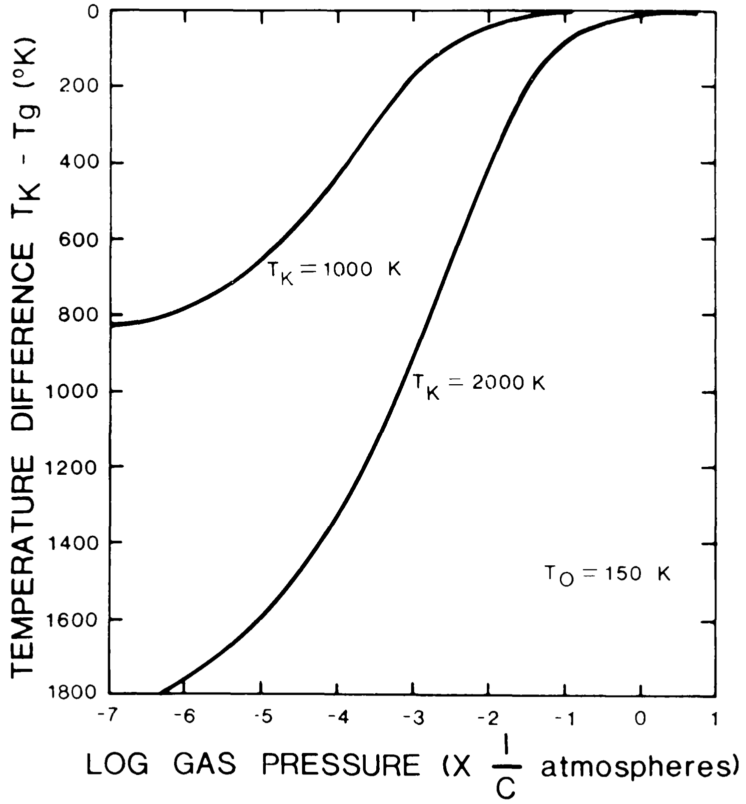

Fig. 3. Degree of temperature disequilibrium as a function of gas pressure (or gas density).

have to far exceed grain opacity for equilibration to occur near the midplane. This appears unlikely (see, e.g., Cameron and Pine, 1973).

Note now that if the grains have come to exist as a result of *in situ* condensation in the nebula, then at the onset of condensation the grain temperature would be represented more realistically by the curve marked T_g (*transparent solution*) – calculated for a transparent nebula – than the curve marked T_g (*convergent solution*), so that disequilibrium would be even more pronounced during early condensation. Furthermore, if condensation occurs as a result of radiative cooling of the gas, then the peripheral regions of the nebula – where disequilibrium is most pronounced – would be a major locale of condensation since cooling would take place more efficiently here than near the midplane. Thus, in the context of the nebular type of condensation scenarios invoked in meteoritics, we may make the general conclusion that condensation favors disequilibrium. The fact that the actual process of condensation of meteoritic material was a thermal disequilibrium phenomenon seems also to be borne out by pertinent observations (see, e.g., Arrhenius *et al.*, this volume).

The above discussion also applies substantially to the case of condensation in expanding shells of supernova and nova ejecta (see, e.g., Clayton, this volume, for a discussion of this case). The expanding gaseous envelopes here are observed to be transparent in the infrared wavelengths, with a resulting temperature disequilibrium

1979Ap&SS..65..191D

of an order of magnitude (see Geisel *et al.*, 1970, and Figure 1 of Arrhenius *et al.*, this volume).

3. Condensation in Disequilibrium: Prigogine Dissipative Structures

Dissipative structures – a concept of nonequilibrium thermodynamics introduced by Prigogine (see, e.g., Prigogine, 1978, and earlier references therein) – are states of organization of matter where disequilibrium becomes a source of order. Higher states of organization can arise within a physical system at the expense of energy dissipated to the environment of the system. As one moves from thermodynamic equilibrium, one expects progressive chaos; however, if one moves sufficiently from equilibrium, one may encounter the Prigogine states where again a tendency to order begins to evolve (see, also, Prigogine, 1979).

Condensation of a vapor into dust grains represents a transition towards a higher state of organization or order. This is especially so when the grains exhibit a crystalline morphology – as is the case for many tangible samples of space condensates represented by meteorites (see, e.g., Wark, 1979). We suggest here the possibility that condensation in space may be a dissipative structure phenomenon, having little to do with the equilibrium state where much of the attention of space condensation studies has been focused to date.

We consider here the case of condensation onto a bulk condensed phase. We thus bypass, for the present purpose, the important problem of nucleation (see, e.g., De and Arrhenius, 1979; De, 1979; and articles by Draine and Herbst, 1979).

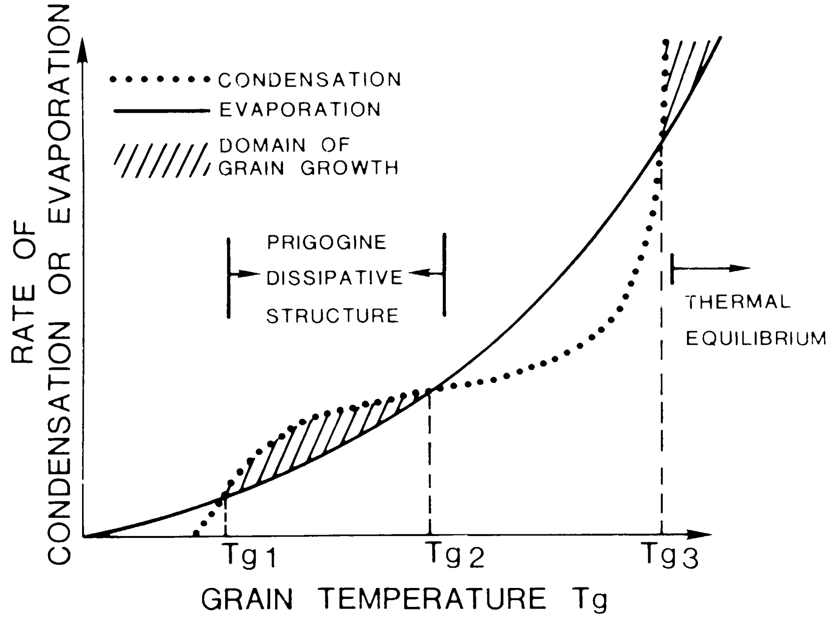

Fig. 4. Rate of condensation or evaporation of molecules as a function of the grain temperature in the state of thermal disequilibrium, showing the temperature domains of grain growth and the emergence of a Prigogine dissipative structure.

Progressive growth of a grain in a state of temperature disequilibrium occurs when the rate of influx of the condensable molecules to the grain surface times their sticking coefficient (i.e., the rate of condensation) exceeds the rate of efflux of the evaporating molecules. The former rate is determined by the gas density and the gas temperature while the latter rate is determined by the grain temperature, where the gas and the grain temperatures are coupled through Equation (1). These two rates are sketched in Figure 4 for a typical substance such as iron (see, e.g., Lehnert, 1970; De, 1973). The two curves intersect at grain temperatures T_{g1}, T_{g2} and T_{g3} which are characteristic of the given substance. The asymptotic increase of the rate of condensation near T_{g3} is associated with asymptotic increase in the gas density, and hence an approach towards equality of T_g and T_k (see Figure 3). Thus the domain of condensation for $T_g > T_{g3}$ represents the conventional equilibrium condensation. As we move towards the left of the diagram, equilibrium is lost, and so is the tendency of the system to proceed towards a higher state of order by condensation. However, if we move sufficiently from equilibrium, then towards the left of T_{g2} we encounter a new state with a revived tendency to order. This is a dissipative structure. Order evolves (i.e., condensation takes place) as the entire dust cloud continues to lose energy to the intercloud medium. From our argument in the previous section, it seems likely that condensation in space occurs through the emergence of such dissipative structures, rather than in equilibrium.

4. Remarks

The simple discussion in this paper suggests that a proper study of the process of condensation in a space environment should include any effects arising from thermal disequilibrium. The concept of dissipative structures may find an important application in this regard. Conversely, by employing this concept, interesting perspectives may be obtained on the condensation process and the condensation environments in space.

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References

Arrhenius, G. and De, B. R.: 1973, *Meteoritics* **8**, 297.
Barshay, S. S. and Lewis, J. S.: 1976, *Ann. Rev. Astron. Astrophys.* **14**, 81.
Cameron, A. G. W. and Pine, M. R.: 1973, *Icarus* **17**, 377.
De, B. R.: 1973, Ph.D. Thesis, University of California, San Diego.

1979Ap&SS..65..191D

De, B. R.: 1977a, *Proc. 8th Lunar Sci. Conf., Suppl. 8 to Geochim. Cosmochim. Acta*, p. 83.
De, B. R.: 1977b, *Proc. 8th Lunar Sci. Conf., Suppl. 8 to Geochim. Cosmochim. Acta*, p. 79.
De, B. R.: 1979, *J. Chem. Phys.* **70**, 2046.
De, B. R. and Arrhenius, G.: 1979, *Advances in Colloid and Interface Science* **10**, 253.
Draine, B. T.: 1979, *Astrophys. Space Sci.* (in press).
Geisel, S., Kleinmann, D. E. and Low, F. J.: 1970, *Astrophys. J.* **161**, L101.
Herbst, Eric: 1979, *Astrophys. Space Sci.* **65**, 13–20.
Lehnert, B.: 1970, *Cosmic Electrodynamics* **1**, 218.
Lewis, J. S.: 1974, *Science* **186**, 440.
Mendis, A.: 1979, *Astrophys. Space Sci.* **65**, 5–12.
Prigogine, I.: 1978, *Science* **201**, 777.
Prigogine, I.: 1979, *Astrophys. Space Sci.*, **65** (in press).